SUMMARY

This thesis deals with the generation and behavior of the azomethine nitrene.

A general introduction (Chapter 1) into the chemistry of nitrenes, summarizing the most pertinent literature is given.

A literature survey of reactions which may involve an azomethine nitrene is presented (Chapter 2). Analysis of literature data revealed a product distribution between 2-phenylbenzimidazole and N,N'-diphenylcarbodiimide, obtained by fragmentation of four different five membered heterocycles to be accounted for by imidazole ring closure from an azomethine nitrene whereas rearrangement concerted with an elimination affords the diimide.

Decarboxylation of Δ^2-1,2,4-oxadiazolin-5-ones was chosen as a source for the generation of azomethine nitrenes. It was realized that the azomethine nitrene could be in equilibrium with its valence isomers, a diazirine believed to be an antiaromatic, and a nitrilimine. The results, obtained on photolysis as well as thermolysis of 3,4-disubstituted-Δ^2-oxadiazolin-5-ones, (3,4-diphenyl-(I), 3-phenyl-4-cyclohexyl-(II), 3-phenyl-4-benzyl-(III), 3-benzyl-4-phenyl-(IV)), strongly support

A good deal of 1,3-dipolar character, due to this electron delocalization, is suggested by the isolation of triazoles (C), believed to have been formed by a 1,3-dipolar cycloaddition reaction of the azomethine nitrene to nitriles, which were also produced by decarboxylation.

The presence of a phenyl group at the azomethine nitrogen, influences the azomethine nitrene to such an extent that the nitrene is highly discriminative toward insertion into any CH bond suitably located, and inserts exclusively into the ortho CH bond of the phenyl group attached to nitrogen with high yield formation of benzimidazoles. A clear demonstration of this behavior was found in the decarboxylation of IV. The influence of the phenyl group can be interpreted either in terms of important contribution of 1.5 dipolar or diradical structures, due to electron delocalization, to the resonance hybrid of the azomethine nitrene, or by the possibility of ring expansion by valence bond isomerization offered by a phenyl group at nitrogen to a diazirine.

The azomethine nitrenes intermolecularly abstracted hydrogens as was indicated by the formation of amidines (A).

It was believed that the ketones, aldehydes, amines and nitriles (group [H]) were produced by fragmentation of the azomethine nitrene or diazirine into a nitrile and a nitrene.

A 1,2-hydrogen shift in benzyl- and cyclohexylnitrene followed by hydrolysis, provides the best explanation for the formation of benzaldehyde(7) and cyclohexanone(5), obtained in the decarboxylation of II and III respectively. Aniline(2), observed in I and IV, was then thought to have been formed from phenylnitrene by a hydrogen abstraction process.

Trimerization of benzaldimine, accompanied by aromatization account for the formation of 2,4,6-triphenyl-1,3,5-triazine(8) and 2,4,5-triphenyl-imidazole(31).

In the photolysis of III, a novel rearrangement was observed, resulting in the formation of the unisolated methylene derivative of N-phenylbenzamidine(23A), followed by hydrolysis to the N-phenylbenzamidine.

It is suggested that carbodiimides (D) and cyanamides (E) are formed by processes other than by a rearrangement in the azomethine nitrene. It is proposed that carbodiimides are produced by a rearrangement concerted with decarboxylation. Although a similar mechanism may be suggested for the formation of cyanamides it was shown that they can also be formed by isomerization of carbodiimides, a novel rearrangement reaction described in Chapter 3.

The synthesis of the virtually unknown nitroso-azomethine derivatives, was of interest, since they might provide a new pathway for the generation of azomethine nitrenes by deoxygenation (Chapter 4).

N-phenylbenzamidoxime was oxidized and dehydrogenated by several reagents to the corresponding nitrosoazomethine, which apparently reacted further with the starting material to form O-benzoyl-N'-phenylbenzamidoxime. A novel 1,3-dipolar addition reaction of benzonitrile oxide with N-phenylbenzamidoxime, presented a new route for the synthesis of O-benzoyl-N'-phenylbenzamidoxime. The use of diethyl azodicarboxylate as a mild and efficient dehydrogenative reagent has been extended to hydroxylamines, and amidoximes.